Mat. Res. Soc. Symp. Proc. Vol. 674 © 2001 Materials Research Society

Magnetic Properties of Transition Metal-Dendrimer Nanocomposites

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ABSTRACT

Magnetic nanocomposites have been successfully prepared by encapsulating nanosized entities of iron, cobalt, and nickel compounds in poly(amido-amine) (PAMAM) dendrimer hosts. Problems related to the instability of the magnetic structures under the influence of an external electromagnetic field have been overcome by using a solid polystyrene matrix to embed the dendrimer hosts containing the magnetic guests. SQUID magnetometry measurements on these nanocomposites showed that after subtraction of the diamagnetic polymer background, at 300 K all samples exhibited paramagnetic behavior, with susceptibilities of 1.14, 1.68, and 0.70×10^{-6} m^3/kg for Fe-, Co-, and Ni-containing samples respectively. The temperature dependence for T<300 K showed typical paramagnetic behavior, with the susceptibility increasing for decreasing temperatures. Curie-Weiss (1/M vs. T) graphs displayed a linear behavior at high temperatures, with temperature axis intercepts (θ) occurring at –139 K (Fe), –16 K (Co), and 0 K (Ni). Negative deviations from Curie-Weiss behavior occurred at T<175 K for the Fe and T<25 K for the Co samples. Magnetic moments calculated from the high temperature Curie constant indicated that Fe, Co, and Ni possessed effective moments of 3.5, 4.4, and $2.8\mu_B$. The negative intercepts and the fact that these moments are larger than those expected for metallic transition metals are indicative that these species are probably present in an oxidized form. The low-temperature behavior indicates either superparamagnetic or soft ferromagnetic behavior.

INTRODUCTION

Recent improvements in the technology for materials preparation, combined with the driving force toward device miniaturization and increased magnetic storage densities, has resulted in the present capability of controlling morphology and features at the nanometer level. Correspondingly, issues relating to magnetism and magnetic anisotropy on a very small size scale have become increasingly important from perspectives of both applied technology and pure science. One of the primary objectives of this study was to develop an understanding of the magnetic behavior of low dimensional systems.

Dendrimers are a relatively new class of three-dimensional, organic molecules consisting of a small linear polymer core, surrounded by consecutive shells of interior branching units called dendritic generations, and culminating with peripheral terminal branch cells. Typically in the size range of 1 to 15 nm, these dendrimers are prepared by a synthetic route which provides exceptional control over the formation and placement of the repetitive branching units, resulting in a well-defined shape, chemistry, and structural symmetry [1-3]. This architecture creates an environment within the dendrimer molecule that facilitates trapping of guest (inorganic) species;

thus they are promising candidates as templates for the formation of polymer/inorganic nanocomposites [4]. The ability to control the size and chemistry of both interior branches and terminal groups (which may be chemically different from the interior), as well as the number of generations, makes it straightforward to manipulate the size of the trapping centers and, correspondingly, the size of the trapped species. Also, because the guest species is essentially encapsulated by the polymer dendrimer, the solubility of the overall nanocomposite is controlled by the dendrimer [5]. Therefore, normally insoluble materials such as semiconductors or metal sulfides, once encapsulated by the dendrimer, can be placed into solution, thus suggesting intriguing biological applications like targeted drug delivery and catalysis.

In recent years, a number of researchers have demonstrated the viability of using dendrimers as templates to contain predetermined numbers/clusters of metal atoms (Cu, Au, Ag, Pt, Pd) [6-10] or other inorganic compounds (CuS, CdS, Ag_2S) [11,12]. This "reactive encapsulation" method, in which the entrapped material is non-covalently bound to the dendritic polymer either by electrostatic or other physical/chemical interactions, or simply by the creation of an interpenetrating polymer network, essentially makes possible atom-by atom control in the construction of nanosized individual domains of materials [9].

Composites of magnetic materials having nanometer dimensions can possess unique properties and property combinations not easily achieved with conventional materials (e.g., both high magnetic permeability and large electrical resistivity). In fact, ferromagnetic behavior itself is strictly related to the cluster size of the individual magnetic entities. Incorporation of magnetic atoms into a dendrimer should prevent unwanted aggregation as well as providing a method for controlling the cluster size. In addition to targeted drug delivery, potential applications for such materials include magnetic imaging pigments, anti-radar coatings, microwave components, and transparent magnetic plastics.

In this work, we have synthesized magnetic-dendrimer nanocomposites of Co, Ni, and Fe. Here, we report on the temperature and field dependence of the magnetization. Ultimately, this work will provide us with a unique opportunity to examine the fundamental nature of ferromagnetism, while developing improved capabilities to engineer magnetic properties at nanometer length scales.

EXPERIMENTAL PROCEDURE

We have successfully prepared magnetic nanocomposites by encapsulating nanosized entities of iron, cobalt, and nickel in poly(amidoamine) (PAMAM) dendrimer hosts. Generation five PAMAM dendrimers were obtained from Dendritech, Inc. and solutions prepared by dispersing metal acetates and dendrimers in a polystyrene matrix. The concentrations of metal in the final matrices were determined by atomic absorption to be 0.10 wt% Fe, 0.38 wt% Ni, and 0.30 wt% Co. Specific details of the sample preparation have been reported elsewhere [9,14]. All samples gave optically clear matrices indicating particle sizes less than 50 nm. Using a solid polystyrene matrix to embed the dendrimer hosts containing the magnetic guests overcame previous problems [13] related to the instability of the magnetic structures under the influence of an external electromagnetic field. SQUID magnetometry measurements were performed in order to characterize the magnetic behavior of the nanocomposites at temperatures from 5 K to 300 K.

RESULTS AND DISCUSSION

Initial magnetization (M) versus applied field (H) measurements were performed at 300 K as follows. A sample consisting of only the dendrimer/polystyrene matrix was first examined to obtain a baseline background signal. It was, as expected, found to be strongly diamagnetic. Then the nanocomposite samples, containing both transition metal and the dendrimer/polystyrene matrix, were measured. The portion of signal due to the diamagnetic matrix was then subtracted out of the latter data, leaving only the magnetic contribution of the transition metal "suspended" within the nanocomposite. This corrected data is plotted in Figure 1. All samples exhibited paramagnetic behavior, with mass susceptibilities calculated to be 1.68, 1.14, and 0.70×10^{-6} m^3/kg for the Co-, Fe-, and Ni-containing dendrimers respectively. From the room temperature susceptibility, effective magnetic moments (μ_{eff}) for the Co, Fe, and Ni in the dendrimers were respectively calculated to be 4.4 μ_B, 3.5 μ_B, and 2.8 μ_B.

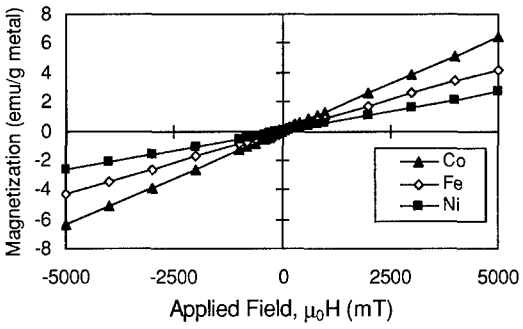

Figure 1. Magnetization versus applied field for the Co, Fe, and Ni components of the dendrimer nanocomposites, showing paramagnetic behavior at 300 K.

The temperature dependence (T<300 K) of the magnetization for the nanocomposites also showed fairly typical paramagnetic behavior, with susceptibility increasing for decreasing temperature, as shown in Figure 2(a). Curie-Weiss (1/M vs. T) graphs of the data [Figure 2(b)] displayed a linear behavior at high temperatures which when extrapolated to low temperatures indicated intercepts (θ) with the temperature axis of –139 K, –16 K, and 0 K for Fe, Co, and Ni respectively. The negative intercept values imply that both the Fe and Co particles exhibit a propensity toward antiferromagnetic interactions, while the 0 K intercept value implies that there are no interactions among the Ni particles in the composite. The slopes of the 1/M vs. T curves were also utilized to calculate effective moments for the Co, Fe, and Ni in the dendrimers. Those values were respectively 4.4 μ_B, 4.4 μ_B, and 2.8 μ_B. Note that the values for Co and Ni agree nicely with those calculated previously, while the 26 % difference in the Fe moment is presumably related to the fact that notable deviations from the linear Curie-Weiss region for Fe begin at temperatures as high as 175 K. This negative deviation from Curie-Weiss behavior also occurred for the Co samples (at T<25 K). Negative deviations from linear Curie-Weiss behavior indicate that either the magnetization is increasing faster than would be expected by the Weiss molecular field, or that the Weiss molecular field is changing with temperature. Since it does not

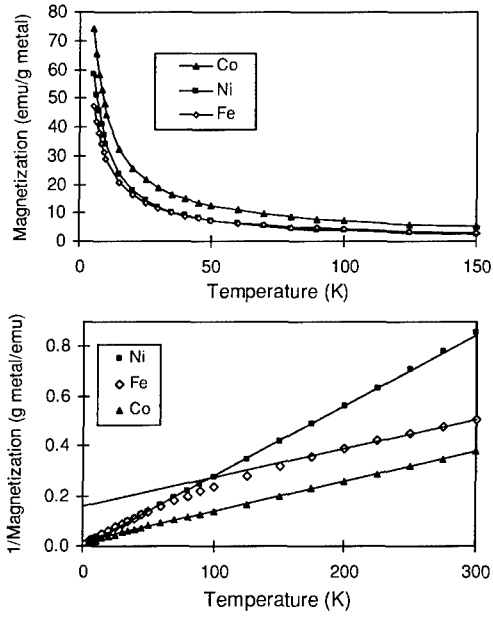

Figure 2. (a) Temperature dependence of magnetization for Co, Fe, and Ni dendrimer nanocomposites measured at constant applied field of 2000 mT while cooling; (b) $(\text{Magnetization})^{-1}$ vs. temperature.

seem unreasonable that the extent of particle/cluster interactions could be changing with temperature, the latter alternative seems more likely. The deviations from linear Curie-Weiss behavior, combined with the negative temperature axis intercepts and the fact that the calculated effective magnetic moments are larger than those expected for metallic transition metals, are indicative that these metallic species are probably present within the composites in an oxidized form.

The low-temperature (T = 5 K) magnetization behavior for these dendrimers is shown in Figure 3. The M vs. H curves begin to approach saturation at fields >3000 mT, and at 5000 mT measured magnetization values are 76, 132, and 123 $A \cdot m^2/kg$ (i.e., emu/g) for Fe, Co, and Ni respectively. However, none of the samples exhibit a measurable coercive field, indicating either superparamagnetic or soft ferromagnetic behavior. Additional analysis and detailed structural characterization is underway in order to resolve this issue.

CONCLUSIONS

Magnetic nanocomposites consisting of iron, cobalt, and nickel entities in polymeric dendrimer hosts have been successfully prepared. SQUID magnetometry measurements on these nanocomposites showed that after subtraction of the diamagnetic polymer background, at 300 K

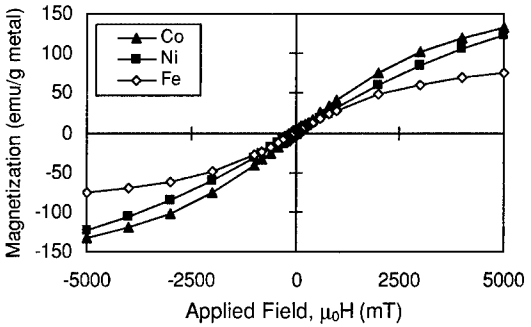

Figure 3. Magnetization versus applied field at 5 K for the Co, Fe, and Ni within dendrimer nanocomposites, showing evidence of superparamagnetic or soft ferroelectric behavior.

all samples exhibited paramagnetic behavior, with susceptibilities of 1.14, 1.68, and 0.70×10^{-6} m^3/kg and effective moments of 3.5, 4.4, and $2.8\mu_B$ for Fe-, Co-, and Ni-containing samples respectively. The temperature dependence for T<300 K also exhibited typical paramagnetic behavior. Curie-Weiss (1/M vs. T) graphs of the data displayed a linear behavior at high temperatures, which when extrapolated to low temperatures indicated intercepts (θ) with the temperature axis of −139 K (Fe), −16 K (Co), and 0 K (Ni). The negative θ values, together with negative deviations from Curie-Weiss behavior, seem to indicate a propensity toward antiferromagnetic interactions in the Fe and Co samples, particularly at lower temperatures. In addition, the fact that the calculated moments are larger than those expected for metallic transition metals is indicative that the metallic species are probably present in an oxidized form. Low-temperature hysteresis measurements exhibit approach to saturation at large fields and no coercivity, thus indicating either superparamagnetic or soft ferromagnetic behavior in these nanocomposite dendrimers.

ACKNOWLEDGMENTS

One of the authors (RAF) would like to acknowledge support from a National Research Council Postdoctoral Research Associateship.

REFERENCES

1. D.A. Tomalia, *Scientific American* **272**, 62 (1995).
2. J.M.J. Frechet, *Science* **263**, 1710 (1994).
3. C. Wu, *Science News* **151**, 384 (1997).
4. L. Balogh, D.A. Tomalia, and G.L. Hagnauer, *Chem. Innov.* **30**, 19 (2000).
5. L. Balogh, D.R. Swanson, R. Spindler, and D. Tomalia, *Polym. Mater. Sci. Eng.* **77**, 118 (1997).

6. L. Balogh and D.A. Tomalia, *J. Am. Chem. Soc.* **120**, 7355 (1998).
7. M. Zhao, L. Sun, and R.M. Crooks, *J. Am. Chem. Soc.* **120**, 4877 (1998).
8. K. Esumi, A. Suzuki, N. Aihara, K. Usai, and K. Torigoe, *Langmuir* **14**, 3157 (1998).
9. L. Balogh, R. Valluzzi, K.S. Laverdure, S.P. Gido, G.L. Hagnauer, and D.A. Tomalia, *J. of Nanoparticle Research* **3**, 1 (1999).
10. F. Gröhn, B.J. Bauer, and E.J. Amis, *Abs. of Papers of the Am. Chem. Soc.* **219**, 295-POLY (2000).
11. N.C. Beck Tan, L. Balogh, S.F. Trevino, D.R. Swanson, D.A. Tomalia, and J.S. Lin, *Polymer* **40**, 2537-45 (1999).
12. K. Sooklal, L.H. Hanus, H.J. Ploehn, and C.J. Murphy, *Adv. Mater.* **10**, 1083 (1998).
13. R.D. Shull, L. Balogh, D.R. Swanson, and D.A. Tomalia, *Abs. of Papers of the Am. Chem. Soc.* **216**, 69-MACR (1998).
14. M.S. Diallo, L. Balogh, A. Shafagati, J.H. Johnson, Jr., W.A. Goddard, III, and D.A. Tomalia, *Environ. Sci. Technol.* **33**, 820 (1999).